ABSTRACT

The possibility for catalytic oxidation of sulfide ions in model solutions of seawater is studied. The catalysts - synthesized metal oxides incorporated in a matrix of activated carbon, are characterized by iodine adsorption. The possibility for using activated carbon as a catalyst is also considered. The influence of the amount of the catalyst is investigated. The experiments are performed at room temperature, with a constant mixing rate and initial concentrations. The oxidation of sulfide ions in the anode compartment of a laboratory scale fuel cell is described. A comparison is made of the oxidation rate into a fuel cell with the catalytical oxidation without electrodes and electrical connections at the same conditions.

Keywords: seawater, sulfide ions, oxidation, catalysts, activated carbon, fuel cell.

INTRODUCTION

Hydrogen sulfide in solution occurs naturally in some thermal springs and closed deep water basins. Black Sea water below a certain a depth, contains significant amount of hydrogen sulfide [1, 2]. The closed nature of the Black Sea creates conditions for its accumulation [2] and this is the reason why the depths of the Black Sea are practically dead except for some sulfur-transforming bacteria. Different methods are used for decomposition of hydrogen sulfide to harmless products [3 - 6]. In many of them the end product is elemental sulfur [3]. From to the literature [2, 7] it is known that metal cations, Me\(^{2+}\) (Me = Mn, Co, Ni, Fe, Cu) catalyze the process. Although Zr is not reported to be a catalyst, experiments with ZrO\(_2\) incorporated into an activated carbon matrix, are also carried out. As the reaction between these metals and the sulfide ions produces a precipitate it is not preferable to add them in a form of salts. Therefore, it was decided to synthesize spinel-type metal oxides, incorporated in a matrix of activated carbon. An additional advantage in this case is that the activated carbon is also a catalyst. This study is part of the efforts to clean up the waters of the Black Sea by oxidation of the sulfide anions of the seawater in a fuel cell (Fig. 1) and to use the energy that is released. The following main reactions are expected to take place in the fuel cell:

Skipping the step of the formation of elemental sulfur is an advantage, because thus is avoided the risk of anode passivation and secondary contamination of the seawater. The sulfate ions occur naturally in seawater and therefore they can be returned to it, restoring the

Fig. 1. Principal scheme of a fuel cell.
cycle of sulfur.

The aim of this work is the selection of a catalyst and the testing of its influence on the oxidation rate of sulfide ions.

EXPERIMENTAL

The model solutions were prepared by dissolving sodium sulfide, nonahydrate (Na₂S.9H₂O reagent ACS ≥ 98 %). It was shown in a previous research that the best oxidation rate of sulfide ions is achieved at a concentration of 60 - 70 mg l⁻¹ [8]. The Black Sea salinity is relatively low (15 - 17 g l⁻¹) [9, 10]. The sea water was simulated by model solutions of NaCl with concentration 16,5 g l⁻¹. The spinel-type catalysts were obtained from organic materials, according to [11]. The procedure includes their impregnation with a solution of pre-determined salt and followed by pyrolysis and simultaneous activation. The catalytic effect is determined by adding them into the volume of the solution.

The experiments were accomplished in the lab-scale fuel cell, shown in Fig. 2. The anodic space is charged with a model solution of sulfide with 200 ml volume. During the runs the solution was agitated by a magnetic stirrer at 300 rpm. The cathode space was charged with the same salt solution, being aerated by atmospheric air with a flow rate 100 dm³ h⁻¹. The concentration of the dissolved oxygen in the cathode compartment of the fuel cell is determined with dissolved oxygen probe, coupled to a pO₂ analyzer. It was established that its concentration was close to the equilibrium one for the experimental conditions (about 95 % vol. of the equilibrium). The anode and cathode spaces are coupled by a salt bridge.

The catalyst was added to the solution in the anodic compartment as a powder. During the runs, samples from the anode space were taken and analyzed for sulfide, sulfur-containing reducing compounds and sulfates. The concentration of all sulfur reducing substances was determined iodometrically. The sulfide (S²⁻) content was determined photometrically [12] and the presence of sulfate ions was determined with barium chloride, after deposition of sulfates. The sulfates were determined by titration of the excess quantity of Ba²⁺ with EDTA in the presence of Eriochrome black T as an indicator.

Experiments for natural oxidation of sulfide ions were also carried out at the same conditions in a stirred flask.

RESULTS AND DISCUSSION

The characterization of the surface of the catalysts was done by adsorption of iodine. The results are given in Table 1.

The surface of the granulated active carbon is about 5 times lower. The experiments with granulated activated carbon are conducted in order to estimate its adsorption properties, but it is also easier to use the granules under real operating conditions.

A comparison of the process of oxidation of sulfide ions in the fuel cell and natural oxidation at the same conditions is shown in Fig. 3 and Fig. 4 with and without catalyst respectively. A catalyst - 0,1 g Co₃O₄, was used.

It can be seen from the figures that the process of oxidation of sulfide ions in a fuel cell is considerably faster.

The catalytic properties of Zr were examined for the

<table>
<thead>
<tr>
<th>Type of the activated carbon matrix</th>
<th>Specific surface, m² g⁻¹</th>
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<tbody>
<tr>
<td>Co₃O₄</td>
<td>897.98</td>
</tr>
<tr>
<td>Zr₂O</td>
<td>780.66</td>
</tr>
<tr>
<td>active carbon granules (Fujikasui, Japan)</td>
<td>145</td>
</tr>
</tbody>
</table>

Table 1. Surface of the used activated carbons.
natural oxidation of sulfides. As shown in Fig. 5 Zr$_2$O demonstrates better catalytic activity than Co$_3$O$_4$. A comparison of the catalytical properties of Zr and commercial granulated carbon is shown in Fig. 6. For commensurability of the surfaces, experiments with a five times greater quantity were also carried out. It can be seen from the figure that even in this case, the Zr incorporated into activated carbon shows better catalytical properties. Another advantage of the use of Zr as a catalyst is that it leads only to sulfates, while in the case of activated carbon there are also other products in the solution. The effect of mixing was also examined. Fig. 7 shows that the mixing significantly influences the oxidation rate of the sulfide ions.

In order to determine the necessary quantity of the catalyst, experiments with different amounts of Zr$_2$O catalyst were carried out (Fig. 8). The figure shows that the sulfide ions are oxidized up to 75% when using 0.1 g catalyst, whereas they are oxidized up to 50% when using 0.05 g of catalyst.
CONCLUSIONS

The process of oxidation of the sulfide ions carried out in the fuel cell is considerably faster. Sulfide ions are oxidized in the fuel cell to 50 % in the second hour without using catalyst and to 20 % when the process of oxidation without a fuel cell is performed. In the presence of a catalyst, sulfide ions are oxidized up to 90 % for the first hour, when using a fuel cell and 60 % - without a fuel cell.

It is proved that the Zr$_2$O can be used as a catalyst for sulfide oxidation leading entirely to sulfates as products.

Mixing influences significantly the oxidation of sulfide ions.

The amount of catalyst does not significantly influence the rate of the reaction for the first hour (Fig. 8). During the second hour the sulfide ions are oxidized up to 95 % with a higher amount of catalyst. Sulfide ions are oxidized up to 60 % upon reducing the amount of the catalyst with 50 %.

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